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(54) **COATING COMPOSITION WITH TRISAMINE  
FUNCTIONALIZED DISPERSANT**

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(2013.01)

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USPC ..... 524/198, 504  
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,731,419	A	3/1988	Fong	
2009/0269510	A1 *	10/2009	Lieberman et al.	427/555
2010/0056668	A1	3/2010	Brown	
2011/0319521	A1 *	12/2011	Lundgard et al.	523/205

\* cited by examiner

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(57) **ABSTRACT**

The present invention relates to a composition comprising a stable aqueous dispersion of polymer particles and a dispersant adsorbed onto the surfaces of TiO<sub>2</sub> particles, wherein the dispersant is a water-soluble polymer functionalized with structural units of a carboxylic acid ester and tris(hydroxymethyl)aminomethane. The composition of the present invention is particularly useful for achieving high hiding for paints containing associative thickeners.

**5 Claims, No Drawings**

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# COATING COMPOSITION WITH TRISAMINE FUNCTIONALIZED DISPERSANT

## BACKGROUND OF THE INVENTION

The present invention relates to a coating composition containing a trisamine functionalized dispersant. The dispersant is useful in promoting hiding in a paint formulation.

Paints containing associative rheology modifiers such as hydrophobically modified ethylene oxide urethane (HEUR), hydrophobically modified alkali soluble emulsion (HASE), and hydrophobically modified hydroxyethyl cellulose (HMEC) thickeners cause latex particles to self-associate, resulting in self-association (crowding) of  $\text{TiO}_2$  particles, thereby reducing hiding efficiency as compared to compositions thickened with non-associative thickeners. This crowding effect occurs because associative rheology modifiers create a network with the binder in the paint system, thereby pushing  $\text{TiO}_2$  particles closer together. It would therefore be desirable to discover a way to improve the hiding efficiency of coatings formulated with associative rheology modifiers.

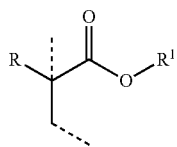
## SUMMARY OF THE INVENTION

The present invention addresses a need in the art by providing a composition comprising a stable aqueous dispersion of polymer particles and a dispersant adsorbed onto the surfaces of  $\text{TiO}_2$  particles, wherein the dispersant is a water-soluble polymer functionalized with structural units of a carboxylic acid ester monomer and tris(hydroxymethyl)aminomethane. The present invention addresses a need in the art by providing a way of improving hiding in a paint formulation thickened with an associative thickener.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention addresses a need in the art by providing a composition comprising a stable aqueous dispersion of polymer particles and a dispersant adsorbed onto the surfaces of  $\text{TiO}_2$  particles, wherein the dispersant is a water-soluble polymer functionalized with structural units of a carboxylic acid ester monomer and tris(hydroxymethyl)aminomethane.

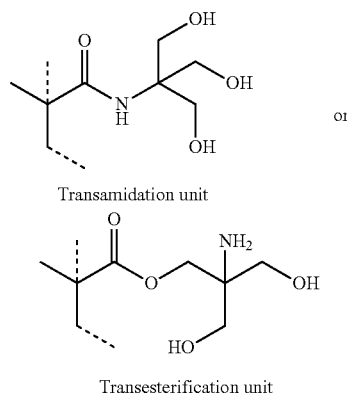
A structural unit of a carboxylic acid ester monomer is illustrated:



where R is H or methyl,  $\text{R}^1$  is a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group, and the dashed lines represent the points of attachment of the unit to the polymer backbone.

A structural unit of tris(hydroxymethyl)methane is represented by a transamidation unit or a transesterification unit or both:

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The dispersant can be prepared by contacting tris(hydroxymethyl)amine with a polymer functionalized with structural units of a carboxylic acid ester monomer, preferably a homopolymer of methyl methacrylate, in the presence of a suitable catalyst such as dibutyl tin oxide in the presence of a high boiling solvent such as N-methylpyrrolidone at an advanced temperature, preferably in the range of 150° C. to 200° C. The dispersant can also be prepared by copolymerizing tris(hydroxymethyl)acrylamide with a carboxylic acid ester monomer such as methyl methacrylate.

The resulting polymer preferably contains both transamidation and transesterification units, preferably at a mole:mole ratio of 2:1 to 10:1 in favor of transamidation; the polymer also preferably contains structural units of unreacted carboxylic acid ester, preferably methyl methacrylate.

Preferably, the mol-to-mol ratio of structural units of tris(hydroxymethyl)methane to structural units of the carboxylic acid ester monomer, preferably methyl methacrylate, is in the range of 40:60 to 90:10. A preferred  $M_w$  for the dispersant is in the range of 1000 to 25,000 g/mol.

The composition of the present invention can be prepared by contacting together the dispersant, the stable aqueous dispersion of polymer particles, and the  $\text{TiO}_2$ . The composition may further include one or more of the following materials: rheology modifiers; opaque polymers; fillers; colorants; other pigments including encapsulated or partially encapsulated pigments and opaque pigments; dispersants; wetting aids; dispersing aids; dispersant adjuvants; surfactants; co-solvents; coalescing agents and plasticizers; defoamers; preservatives; anti-mar additives; flow agents; leveling agents; slip additives; and neutralizing agents.

In the following examples, polymethylmethacrylate was obtained from Aldrich and was reported to have an  $M_w$  of ~15,000 g/mol (Example 1) and ~5300 g/mol (Example 2).

## EXAMPLES

### Example 1

#### Preparation of Poly(methyl methacrylate)-g-Tris(hydroxymethyl)aminomethane

Polymethylmethacrylate (20 g,  $M_w$ =15,000 g/mol as supplied by Aldrich), tris(hydroxymethyl)aminomethane (70 g), N-methyl-2-pyrrolidone (NMP, 40 mL) and dibutyl tin oxide (500 mg) were mixed and heated to 190-200° C. in a reaction flask equipped with a reflux condenser for 2 h. The product was cooled and precipitated in diethyl ether, then dried at in

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vacuo 60° C. This polymer was reprecipitated by dissolution in NMP and precipitating in diethyl ether, then re-dried at 60° C. in vacuo.

## Example 2

## Preparation of Poly(methyl methacrylate)-g-Tris(hydroxymethyl)aminomethane

The procedure from example 1 was followed substantially as described except that a polymethylmethacrylate having a  $M_w$  of 5,300 g/mol was used.

## Paint Formulation

Paint formulations were prepared using Examples 1 and 2 as well as a comparative formulation using TAMOL™ 2002 Dispersant (a hydrophobic polyacid copolymer). In the following Table 1, TiO<sub>2</sub> refers to Ti-Pure R-706 TiO<sub>2</sub>, SG-10M refers to RHOPLEX™ SG-10M Acrylic Copolymer, Texanol refers to Texanol Coalescent, RM-2020 refers to ACRY SOL™ RM-2020 NPR Rheology Modifier, RM-825 refers to ACRY SOL™ RM-825 Rheology Modifier, and 15-S-9 refers to TERGITOL™ 15-S-9 Surfactant. (TAM-POL™, RHOPLEX™, ACRY SOL™, and TERGITOL™ are all Trademarks of The Dow Chemical Company or its Affiliates.)

TABLE 1

Paint formulation Using Example 1 or Example 2 Dispersant	
	Weight (g)
Grind	
Dispersant (dry)	0.07
Water	1.68
TiO <sub>2</sub>	4.69
Grind Sub-Total	6.44
Letdown	
SG-10M	13.94
Texanol	0.56
Water	3.55
RM-2020	0.56
RM-825	0.015
15-S-9	0.1
Letdown sub-total	18.72
Total	25.16

The paints were coated on a Leneta chart and Hiding (S/mil) was determined using the Kubelka-Munk S/mil Test Method.

## Kubelka-Munk S/mil Test Method:

Two draw-downs were prepared on Black Release Charts (Leneta Form RC-BC) for each paint using a 1.5-mil Bird draw down bar and the charts allowed to dry overnight. Using a template, 3.25"×4" rectangles were cut out with an X-ACTO knife on each chart. The Y-reflectance was measured using a BYK Gardner Spectro-guide 45/0 Gloss Color spectrophotometer in each of the scribed areas five times measuring on a diagonal starting at the top of the rectangle and the average Y-reflectance recorded. A thick film draw

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down was prepared for each paint on Black Vinyl Charts (Leneta Form P121-10N) using a 3" 25 mil block draw down bar and the charts were allowed to dry overnight. The Y-reflectance was measured in five different areas of the draw down and the average Y-reflectance recorded. Kubelka-Munk hiding value S is given by Equation 1:

$$S = \frac{R}{X \times (1 - R^2)} \times \ln \frac{1 - (R_B \times R)}{1 - \frac{R_B}{R}} \quad \text{Equation 1}$$

where X is the average film thickness, R is the average reflectance of the thick film and  $R_B$  is the average reflectance over black of the thin film. X can be calculated from the weight of the paint film ( $W_{pf}$ ), the density (D) of the dry film; and the film area (A). Film area for a 3.25"×4" template was 13 in<sup>2</sup>.

$$X(\text{mils}) = \frac{W_{pf}(\text{g}) \times 1000(\text{mil/in})}{D(\text{lbs/gal}) \times 1.964(\text{g/in}^3 / \text{lbs/gal}) \times A(\text{in}^2)}$$

The hiding values for the formulated paints are shown in Table 2.

Example No.	Dispersant in Paint Formulation	S/mil
Example 1	PMMA-Tris $M_w$ = 15 K	6.54
Example 2	PMMA-Tris $M_w$ = 5.2 K	6.52
Comparative 1	TAMOL 2002 Dispersant	5.64

The results demonstrate that excellent hiding can be achieved in paint formulations containing an associative thickener (in these examples, a HEUR thickener) using the PMMA-Tris dispersants of the present invention.

## The invention claimed is:

1. A composition comprising a stable aqueous dispersion of polymer particles and a dispersant adsorbed onto the surfaces of TiO<sub>2</sub> particles, wherein the dispersant is a water-soluble polymer functionalized with structural units of a carboxylic acid ester and tris(hydroxymethyl)aminomethane.

2. The composition of claim 1 wherein the carboxylic acid ester is methyl methacrylate.

3. The composition of claim 2 wherein the mol-to-mol ratio of structural units of tris(hydroxymethyl)aminomethane to structural units of methyl methacrylate is in the range of 40:60 to 90:10.

4. The composition of claim 1 which further includes an associative thickener.

5. The composition of claim 1 which further includes one or more materials selected from the group consisting of rheology modifiers; opaque polymers; fillers; colorants, other pigments including encapsulated or partially encapsulated pigments and opaque pigments; dispersants; wetting aids; dispersing aids; dispersant adjuvants; surfactants; co-solvents; coalescing agents and plasticizers; defoamers; preservatives; anti-mar additives; flow agents; leveling agents; slip additives; and neutralizing agents.

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